

Ink-jet Printed BaTiO₃ for Photonics

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ABSTRACT

A water-based BaTiO₃ precursor solution, suited for ink-jet printing of hetero-epitaxial BaTiO₃ layers on LaAlO₃ single-crystal substrates was developed. First, a study on the simultaneous stabilization of Ba²⁺ and Ti⁴⁺ ions in a neutral, aqueous environment was performed. Thermal analysis of the precursor was used to select appropriate temperature programs and the rheology of the solutions is studied to optimize dipcoating and later ink-jet printing parameters. On both substrates, it was possible to obtain epitaxial layers of about 200 nm thickness after sintering at temperatures above 1000 °C. Currently, we are adapting the thermal program and heating atmosphere in order to reduce the sintering temperatures, decrease the surface roughness and increase density.

INTRODUCTION

Ferro-electric materials find application in capacitors, piezo-electric actuators, DRAM memory devices, electro-optic components etc. Probably the most innovative application for ferroelectrics is their incorporation in photonics. Yet, integration of metaloxides on Si-based components remains an area of research with much room for improvement in terms of materials processing. Theoretically, BaTiO₃, having a very high opto-electronic coefficient, remains one of the most promising materials for use as opto-electronic modulator. Yet, there are some important restrictions hindering its' practical use. To reduce optical losses and ensure high modulating efficiency, we need to integrate quasi single crystalline BaTiO₃ (BTO) with perfect epitaxy and extremely smooth surfaces with Si technology. Currently, these requirements can only be fulfilled by other materials with an intrinsic lower opto-electric coefficient such as LiNbO₃ and PbZr_{1-x}Ti_xO₃ or by using PLD, CVD or MBE to deposit BaTiO₃ [1,2].

Chemical solution deposition (CSD) combined with ink-jet printing provides a very valuable alternative, holding the promise of cheap, fast and scalable processing. Patterns can be obtained directly without etching and the approach can be compatible with a whole series of materials and even graded materials [3-7]. Reports on CSD of epitaxial BaTiO₃ are scarce [8-11]. Therefore, this work started with the formulation of an environmentally-friendly, aqueous Ba-Ti precursor solution suited for dipcoating on LaAlO₃ (LAO) single crystals. Thermal treatment at temperatures above 1000 °C results in epitaxial BTO layers. The precursor rheology and wetting behaviour was studied to confirm compatibility with the inkjet printing devices and printing tests were performed. Similar precursor solutions as the ones used here were used before to produce a complete multiferroic structure of BTO/LSMO on STO by ink plotting [4].

In the future, further optimization of the thermal treatment procedure and wettability of the precursor should allow to transfer the procedure for deposition on MgO single crystals and optimization of the density and smoothness of the layer should further improve its performance. In this way, our BTO layers can be integrated in a Mach-Zehnder configuration allowing testing of its light guiding and modulating performance [12-15].

EXPERIMENT

Aqueous BaTiO₃ precursor solutions were obtained by mixing stoichiometric amounts of separate Ba²⁺ and Ti⁴⁺-solutions set at identical pH levels. As titanium precursor, titanium-isopropoxide (Sigma-Aldrich) is used. To prevent the Ti⁴⁺ from hydrolyzing upon contact with water, the alkoxide is stabilized by mixing it with triethanolamine (TEA, Fluka) in a 1:2 molar ratio. After this, water (Sigma-Aldrich) is added to obtain a 1M Ti⁴⁺-solution (see [16] for more details on ink-jet printing of aqueous Ti⁴⁺-precursor). Stable 1M Ba²⁺-solutions can be obtained by adding Ba(NO₃)₂ (Alfa Aesar) to an iminodiacetic acid (IDA, Alfa Aesar)/ethanolamine (EA, Sigma-Aldrich) solution. This IDA solution is prepared by adding iminodiacetic acid to about half of the volume of water necessary to obtain a final composition of 1M of Ba²⁺ ions, with a Ba/IDA ratio of 1:3. Then, EA is added to the IDA/water mixture until all of the IDA is dissolved. To ensure correct weighing, the hydrate number of the Ba-salt is determined by TGA analysis. Stoichiometric volumes of the two separate solutions are mixed and a small amount of EA is added to set the pH to 7. Finally, water is added to obtain the correct concentration. For some experiments, the precursor was further diluted to 0.25M BTO. All BTO precursor solutions have a shelf life stability of a few days and result in clear gels, the separate Ba and Ti solutions have a much longer shelf life. Dilution clearly has a positive effect on the precursor stability and increases the shelf life of both precursor solutions and gel.

To convert the precursor solution to BTO powder the following steps are performed : first, the solution is gelled at 60 °C for 2h. Subsequently, calcination is performed by heating the gel at 3°C/min to 475°C, dwelling for 1 hour, further heating to 1100 °C at 5°C/min and again dwelling for 1.5h. The sample is left to cool in the tube furnace, and the entire thermal treatment is performed under full oxygen atmosphere to promote burn-off of all organics and avoid reduction of the powder leading to purple coloration typical of oxygen deficient titania polymorphs. For the deposition of thin films, 1 mm thick, 1x1 cm single crystal LAO or STO single crystals (Crystec, Germany) are used. Prior to coating, the substrates are rinsed in isopropanol to remove organics from the surface and heated to 400 °C directly on a hotplate to thermally clean the surface. The precursor is dipcoated (KSV instruments) 50 mm/min in a clean room environment (class 100). After coating, the wet layers are left to dry at 60 °C for 30 min and then submitted to the same thermal treatment as for the powders. The substrates were coated at room temperature using a piezoelectric DOD ink-jet system (MicroFab Technologies, MJ-ABP-01-30) with a 30 µm orifice diameter and an XY positioning system under computer control. The ink was filtered with a 0.2 µm pore size PET filter before printing.

The thermal decomposition behavior of the precursor was studied by thermogravimetric and differential thermal analysis (TG-DTA), using a NETZSCH STA 449 F3 Jupiter®. To avoid excessive weight losses below 100 °C, the solutions are converted into gels by heating them at 60°C prior to TGA analysis. The crystallinity of the powders was determined from X-ray diffraction (XRD) analysis (Thermo Scientific, ARL X'TRA) as well as the texturation and phase purity of the films (Bruker, D8). Infra red (IR) spectroscopy was used to identify the presence of BTO and undesired side phases (DRIFT - Thermo 6700 FLEX FTIR/FT-Raman instrument). Determining the layer thickness of a transparent layer on a transparent substrate is very hard, and optical profilometry and ellipsometry failed in our case to generate reproducible results. Therefore, focused ion beam-scanning electron microscopy (FEI Nova 600 Nanolab

Dual-Beam FIB) was used to directly determine the thickness from cross-sectional views and to study the morphology inside the layer. Atomic force microscopy (AFM, Molecular Imaging, PicoPlus) is used to determine the thickness of the printed tracks and surface roughness. The viscosity of each solution was determined using a Brookfield DVE viscometer. To assess the wettability of the substrate, the contact angle of a 10 μl droplet of precursor solution on LAO single crystal is determined, as well as the surface tension by the pendant drop method using an optical tensiometer (Krüss DSA30).

DISCUSSION

Precursor : thermal analysis

Figure 1a shows data from TGA/DTA analysis performed for a 0.5 M aqueous BTO precursor formulated as described in the experimental section. Until 250 $^{\circ}\text{C}$, water and ethanolamine (bp = 170 $^{\circ}\text{C}$) evaporate from the gel, as evidenced the large weight loss of over 50%. A large exothermic DTA peak between 250 and 650 $^{\circ}\text{C}$ indicates the further decomposition of the precursors, consisting of two main steps in the TGA signal. It is generally accepted that BTO is formed from reaction between TiO_2 and BaCO_3 or from an intermediate such as $\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3$ for aqueous sol-gel precursors [11, 17, 18]. Given most of the reaction is complete by 650 $^{\circ}\text{C}$, we believe that the mixed intermediate can play a role here since BaCO_3 reacts only at much higher temperature. Between 600 $^{\circ}\text{C}$ and 800 $^{\circ}\text{C}$ further minor and gradual weight losses are observed indicating further loss of carbonates.

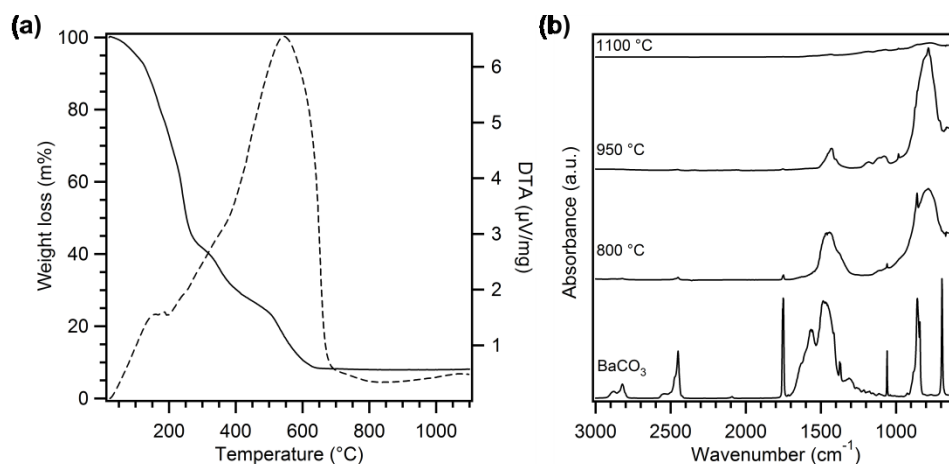


Figure 1. (a) TGA/DTA data collected for a BTO gel by heating under air at 5 $^{\circ}\text{C}/\text{min}$. (b) IR spectra collected for BTO gels heated at different temperatures and pure BaCO_3 powder.

Although the decomposition mechanism is not completely clear, IR measurements clearly evidence the formation of BaCO_3 ($\delta_{\text{ip}} = 693$, $\delta_{\text{oop}} = 857$, $\nu_s = 1059$ and $\nu_s + \delta_{\text{ip}} = 1750 \text{ cm}^{-1}$) while a paper on the mixed oxycarbonate intermediate claims $\delta_{\text{oop}} = 875 \text{ cm}^{-1}$. XRD analysis of a powder heated to 950 $^{\circ}\text{C}$ confirms the IR data and evidences the formation of orthorhombic BaCO_3 and tetragonal BTO as main phase, with some unidentified side phases, the most important exhibiting an intense, doubled reflection at $2\theta = 28.8\text{-}29.4$ (Figure 2a). After heating at 1150 $^{\circ}\text{C}$, the BaCO_3 disappeared, and pure BTO is obtained, with still small contamination of the unidentified side phase.

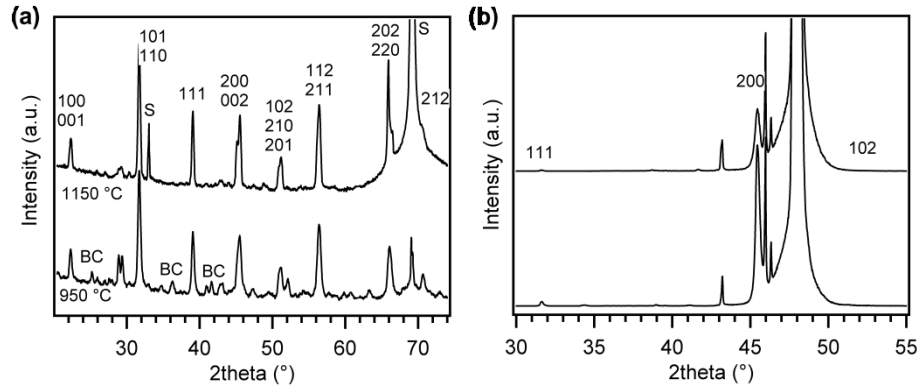


Figure 2. XRD spectra collected for (a) bulk BTO powder after heating to 950 and 1150 °C (sample holder peaks are indicated with S) and (b) BTO thin films on LAO obtained by dipcoating or ink-jet printing.

Precursor : wettability, printability

In order to use BTO in photonics, we need to be able to deposit epitaxial layers of the material. Therefore, we use our aqueous precursor to dipcoat and ink-jet print on LAO single crystal substrates. To ensure proper wetting and jetting behavior, we determined the rheological properties of the solution. The viscosity is 4.11 mPa.s at room temperature, the surface tension from pendant drop measurement is 47.9 mN/m. The contact angle on LAO substrates is below 5° and therefore cannot be exactly determined. These values are within the range suited for dipcoating, yet the requirements for proper jetting behavior are more strict. The behaviour of inks in the printing system can be quantified by a number of dimensionless groupings of physical constants, of which the Ohnesorge (Oh) number is the most relevant :

$$Oh = \frac{\eta}{\sqrt{\rho\sigma r}} \quad (1)$$

with σ , ρ , η and v the ink surface tension (J.m⁻²), density (kg.m⁻³), viscosity (Pa.s) and velocity (m.s⁻¹) respectively and r the diameter of the orifice of the nozzle (m). Often it is written that Oh⁻¹ should be between 1 and 10 for proper jetting properties. If the ratio is too low, viscous forces become more dominant preventing drop ejection; conversely, if the ratio is too high the possibility for satellite droplet formation becomes high [6, 19]. Based on a density of 1.13 g/mL, we find Oh⁻¹ = 9.8 for our BTO precursor solution, which means it should be suited for jetting.

Both dipcoating and ink-jet printing were used to prepare thin BTO coatings on LAO substrates. Dipcoating at 50mm/min of a 0.5 M BTO solution results in a homogenous, transparent film (Figure 3a). To obtain fully covered substrates by ink-jet printing, we used the following experimental parameters : jetting frequency = 1 kHz, the drive voltage for ejection = 25V, we print two layers in a unidirectional raster pattern with the inter droplet distances optimized to 0.05 mm (longitudinal) and 0.08 mm (lateral). By changing the printing patterns tracks could be printed (single coat). This is an important results since being able to produce patterned BTO deposits without an additional etching step creates an important added value for the CSD ink-jet printing approach compared to the classical used methods. In Figure 3a, digital pictures of a full BTO jetted coating and BTO tracks printed on LAO after complete thermal

treatment are shown.

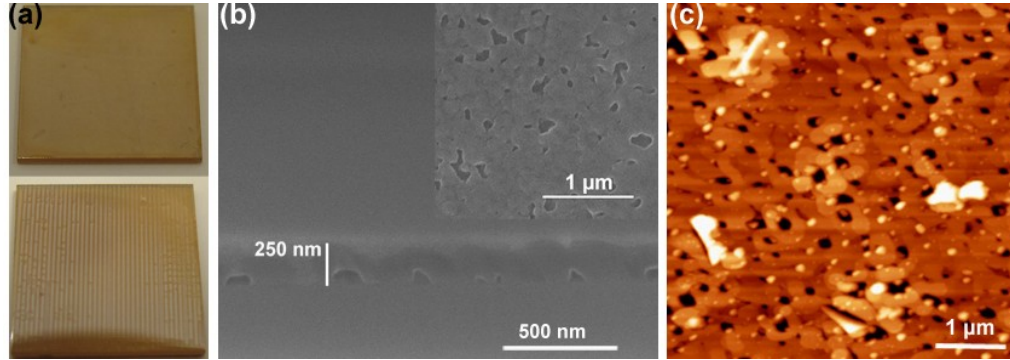


Figure 3. (a) digital pictures of a BTO film and BTO tracks, (b) FIB-SEM cut obtained for a dipcoated BTO layer, inset : surface view for the same sample and (c) AFM topography collected for a printed BTO film.

Thin films : epitaxy and morphology

For applications in photonics, a number of primary criteria need to be fulfilled by the BTO coatings : (1) perfect epitaxy, (2) smooth surface, (3) appropriate thickness (± 200 nm for first tests) and (4) preferably columnar morphology with small amount of pores and grain boundaries, in order to ensure suppression of optical losses and high modulation frequencies [1,2,20,21]. In Figure 2b, we show the XRD results obtained for dipcoated and printed BTO films on LAO. Clearly, for both samples, the (002) reflection is the most intense, while only a very weak (111) reflection can be seen. From FIB-SEM cross sectional view, we find that for a dipcoated sample, the BTO layer is approx. 250 nm thick (Figure 3b), for the printed samples, somewhat thinner layers of 150 nm were found. Holes are present on the surface (Figure 3b inset) as well as at the LAO/BTO interface, an issue that should be resolved by optimizing the thermal treatment. The BTO tracks are approx. 150 μm wide, the thickness of the tracks is determined to be 120 nm on the edges and 50 nm in the middle of the track, an obvious result of the well-know coffee-ring effect by measuring AFM over the track/substrate step. Finally, AFM was also used to determine the roughness of the films, generating an RMS ($5 \times 5 \mu\text{m}^2$) value of 24 nm for the dipcoated films and 15 nm for the printed films. On the edges of the substrate, where the layer is thicker, the roughness of the printed layer is significantly higher.

CONCLUSIONS

The aqueous BTO precursor solution developed in this work fulfills all rheological criteria for piezo-electric inkjet printing and dipcoating on LAO single crystal substrates. Both deposition techniques result in homogeneous, transparent and hetero-epitaxial BTO films with a thickness of 250 nm. By using ink-jet printing, not only complete films but also 150 μm wide tracks can be deposited. The dipcoated films have a surface roughness of 24 nm, while the printed films, which are slightly thinner (150 nm) have a smoother surface with an RMS value of 15 nm.

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